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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C07C 45/29, B01J 27/188, 31/34	A1	(11) International Publication Number: WO 94/21583 (43) International Publication Date: 29 September 1994 (29.09.94)
(21) International Application Number: PCT/GB94/00441 (22) International Filing Date: 8 March 1994 (08.03.94) (30) Priority Data: 9305234.8 13 March 1993 (13.03.93) GB (71) Applicant (for all designated States except US): SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): BROWN, Scott, William [GB/GB]; 105 Rectory Lane, Standish, Wigan WN1 2TY (GB). (74) Agent: PEARCE, Timothy; Solvay Interox Limited, Patent Department, P.O. Box 51, Moorfield Road, Widnes WA8 0FE (GB).		(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: OXIDATION OF ALCOHOLS (57) Abstract A process for the selective oxidation of alcohols to aldehydes or ketones is provided. The process is particularly suitable for the oxidation of alcohols containing other oxidation-sensitive groups such as carbon-carbon double bonds. The process employs a tungsten-containing heteropolyacid catalyst supported on an insoluble particulate support. Preferably, the heteropolyacid contains phosphorus, and the preferred support comprises activated alumina.		

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Oxidation of Alcohols

This invention concerns the oxidation of alcohols. More specifically, this invention concerns the selective oxidation of alcohols to aldehydes or ketones.

In the field of organic chemistry the oxidation of alcohols to carbonyl compounds is often effected either to produce a particular desired product or to allow further conversion to other products or intermediates. The presence of a carbonyl group, and in particular an aldehyde or a ketone group, permits a much wider variety of possible further transformations than does an alcoholic group. Unfortunately, and particularly in the case of aldehydes, the carbonyl group itself is highly susceptible to further oxidation under the conditions employed to oxidise the alcohol, and often further oxidation to carboxylic acids can occur. Although such products may be required in certain situations, it is often desirable that the oxidation proceeds only to the intermediate carbonyl compound. Because of the relative difficulty in producing them, such intermediate products can have a higher unit value than the corresponding carboxylic acid. An oxidation system that allows selective and controlled oxidation to these intermediate carbonyl compounds would therefore be advantageous.

One oxidant that is sometimes desirable to employ in the oxidation of alcohols is an aqueous solution of hydrogen peroxide, because it is relatively cheap, easy to handle and is environmentally acceptable in that its decomposition products are water and oxygen. In order to achieve effective alcohol oxidations with hydrogen peroxide, it has often been found necessary to employ a catalyst. Such catalysts are commonly based on transition metals, and are often employed as homogeneous catalysts i.e. they are employed in the same phase and/or physical state as the reagents. For example, in their article in the Journal of Organic Chemistry, 1988 Vol 53 pp3587 to 3593, Yasutaka Ishii et al propose the use of heteropolyacids or

their salts under phase transfer conditions to catalyse the ketonisation of alcohols. Although the use of homogeneous catalysts commonly has the advantage of a relatively high rate of reaction compared to other forms of catalyst, one drawback of such an approach is that the reaction depends on the formation of a solution of the catalyst, which is then brought into contact with the alcohol. This means that on completion of the reaction, the catalyst often remains in solution. Such a solution can, in theory, be separated from the reaction product and recycled, but in many cases, particularly where the product is a liquid, this process can involve a distillation stage. It is widely recognised that the distillation of a solution which may contain peroxide residuals is a potentially hazardous operation because the potential concentration of peroxides can result in the formation of explosive compositions. In order to mitigate against such hazards, solutions which may contain peroxide residuals are often chemically treated, typically with a reducing agent such as sodium thiosulphate solution, to remove any peroxide residuals. Unfortunately, such a chemical treatment can alter the chemical nature of catalyst remaining in solution, particularly in the case of relatively complex catalysts such as heteropolyacids, and this can mean that the activity of the catalyst is lost or significantly reduced when the solution is recycled, thereby rendering the recycling ineffective.

An alternative to recycling is to dispose of such solutions to waste, but such disposal is becoming increasingly regulated and correspondingly more expensive. In addition, such a disposal also represents a significant chemical cost because of the loss of chemicals, and particularly for relatively expensive transition metals. It has therefore become expedient to recover spent catalyst if possible, notwithstanding the problems outlined hereinbefore, but where the catalyst is in solution, such recovery can involve the construction and operation of relatively expensive separation plants. It is therefore desirable to identify a process for the oxidation of alcohols with hydrogen peroxide that employs a catalyst that can be relatively easily separated from the reaction medium.

In order to improve recovery of the catalyst, one approach that can be contemplated is to employ a heterogeneous catalyst. As the majority of reaction systems employed are liquid, such heterogeneous catalysts are most commonly solids. However, if a catalyst is present in a different physical form to the reagents, the amount of intimate contact between them is reduced, and this can result in the rate of reaction being unacceptably low, or even in there

being no reaction. It is therefore desirable that the heterogeneous catalyst employed does not result in an unacceptably slow reaction.

A further potential disadvantage is that many catalysts which oxidise alcohols can also oxidise ketones and particularly aldehydes so that it is
5 difficult to control the extent of oxidation.

Accordingly, it is an object of the present invention to provide a process for the oxidation of alcohols which permits controlled and selective oxidation to aldehydes or ketones.

It is another object of some or further embodiments of the present
10 invention to provide a process for the selective oxidation of alcohols with hydrogen peroxide in the presence of a catalyst that can be separated relatively easily from the reaction medium.

It is yet another object of the present invention in at least some
embodiments to provide a process for the selective oxidation of alcohols with
15 hydrogen peroxide in the presence of a catalyst that can be separated relatively easily from the reaction medium that does not result in an unacceptably slow reaction.

According to the present invention, there is provided a process for the selective oxidation of alcohols wherein a substrate alcohol is contacted with
20 hydrogen peroxide in a reaction medium in the presence of catalyst, characterised in that:

i. the reaction medium comprises a solvent that does not comprise a carboxyl group, and

ii. the catalyst comprises a heteropolyacid which is supported on an
25 insoluble particulate support.

In the process according to the present invention, the catalyst contains a non-metallic heteroatom which may be selected from Group IV including silicon and germanium or Group V including phosphorus. Preferably, the catalyst contains phosphorus as the non-metallic heteroatom.

30 Tungsten or molybdenum, preferably tungsten, may constitute the entire metallic component of the heteropolyacid. Two transition metals, such as tungsten and molybdenum, may be incorporated therein. Many heteropolyacids for employment in the present invention process can be represented by the empirical formula $Q_{3/n}PW_wMo_{12-w}O_{40}$ when they are
35 brought into contact with the support in which w represents 0 or an integer of at least 1 and often at least 6. Most preferably, w represents 12. Q represents hydrogen or other counterion, and n is its basicity in the general formula. It is believed that the supported catalyst retains its empirical ratio of

tungsten to phosphorous and molybdenum, but that the interaction of the catalyst with the surface of the support may result in the catalyst becoming bonded chemically to the support, thereby modifying both the catalyst itself and the support surface. Such treatments may also encourage a redistribution
5 of the metal between species of different nuclearity.

Other heteropolyacids contemplated for use in the present invention include those containing at least one first series transition metal, including specifically iron, manganese, cobalt and nickel, for example in heteropolyacids of the formula $Q(7-v)/nPW_{11}MxO_{36+v}$ in which Mx represents the other
10 transition metal, v is its oxidation state and Q is the counterion of basicity n as before.

The support for the heteropolyacid catalyst is often selected from solids of Group IIa, IIb, IIIb, IVa and IVb elements and from organic basic ion exchange resins. Within the class of Group IIa compounds, it is often
15 convenient to select as support from magnesium compounds, including in particular, magnesium oxide and magnesium silicate. Within the class of group IIb compounds, it can be convenient to select from zinc compounds as support, including specifically zinc oxide. Within the class of Group IVa compounds, it is often convenient to select from titanium or zirconium
20 compounds, including specifically titanium oxide and zirconium phosphate. From within the class of inorganic Group IVb compounds, it is often desirable to select as supports from tin compounds, many of which are readily available, or from germanium compounds. Specific examples include tin oxide.

25 For the avoidance of doubt, the division herein of the Elements of the Periodic Table into Groups a and b is that employed by F A Cotton and G Wilkinson in Advanced Inorganic Chemistry (2nd Edition) published by Interscience (John Wiley and Sons).

In a number of preferred embodiments, the catalyst support is selected
30 from Group IIIb compounds, especially from non-sintered oxides, and particularly from aluminium compounds. An especially suitable support comprises an activated alumina, including in particular, gamma alumina. For the avoidance of doubt, the term activated alumina refers to non-sintered alumina obtainable by calcining alumina or aluminium hydroxide at
35 temperatures below that at which sintering occurs, and includes specifically the products obtained by calcining at around 400 to 600°C. The alumina may already be present in the activated form at the time of contact with the

catalyst or alternatively neutral alumina or aluminium hydroxide may be converted into activated alumina by a post-impregnation calcination step.

- The organic support can be selected from strong base ion exchange resins. Such resins typically comprise a cross-linked polystyrene, the cross
- 5 linking monomer often comprising divinylbenzene in a small fraction of the monomer mix such as 1 to 2 mole %, the benzene nucleus in the styrene being substituted by an organic base, particularly by an alkyleneammonium group. Examples of possible ammonium groups include
- alkylenetrialkylammonium, often methylenetrimethyl-ammonium or the
- 10 corresponding groups in which one or more of the methyl groups are replaced by another short chain alkyl such as ethyl and/or one of the alkyl groups being hydroxyl-substituted, as in methylenedimethylhydroxyethylammonium group. Other suitable anion exchange resins include insoluble polyacrylic resins in which the carboxylic acid function is further substituted by an
- 15 alkyleneammonium group, for example ethylenetrimethylammonium. The ion-exchange resin can be selected from micro or macro-reticulated strongly basic resins. Naturally, the invention does not encompass so calcining any organic resin after impregnation with the heteropolyacid solution that it is structurally harmed.
- 20 The support is usually employed in the form of discrete particles, the particle size range often being selected such that the supported catalyst particles are distributed through the reaction mixture to a substantial extent during the agitation of the mixture. A convenient average particle size often lies in the range of from about 100 microns to about 5 mm.
- 25 The catalyst can be introduced to the support most conveniently in solution in a suitable solvent, which can comprise water or a polar organic solvent such as a low molecular weight aliphatic alcohol or a mixture thereof. Low molecular weight herein indicates up to C4 (butanols). The solution can, in principle, contain any concentration of catalyst up to and including a
- 30 saturated solution, and in preference is at or near saturation, so as to minimise the volume of solvent that is subsequently removed. The solution can be contacted with the support in bulk until a desired amount has been absorbed and after separation from the liquid phase, the impregnated support is thereafter dried and can then be calcined. Calcination is a preferred stage if
- 35 an impregnation stage has been employed. The impregnation contact period often lasts from about 30 minutes to 8 hours. In a variation, the support may be charged into a column through which a solution of the heteropolyacid is

permitted to percolate, preferably with recycle of the eluate to maximise uptake of the catalyst from the solvent.

The contact may be made at or around ambient temperature, which is typically in the region of from about 15 to 25°C or it may be conducted at an elevated temperature up to the boiling point of the solvent under the selected pressure conditions. By employing an elevated temperature, and particularly one that is within 10°C of the solvent boiling point, the solvent is evaporated away to at least some extent during the contact period. Once the solution has reached saturation, any further solvent removal results in the catalyst being deposited on the support. Accordingly, the support can thereby be loaded with a higher level of catalyst than is obtainable by simply impregnating the support with a saturated solution, separating the support from excess liquor and drying. Particularly for use in conjunction with solvent evaporation during the contact phase, the solvent is methanol or an alternative low boiling point solvent.

The extent of loading of the catalyst is to at least some extent at the discretion of the user. It is often convenient or desirable to employ a loading of from about 4 to 30% by weight of the catalyst, calculated as the metal, based on the dry weight of the support. In a number of effective embodiments the catalyst loading is between 5 and 17% by weight of the dry weight of the support.

During calcination of the supported catalyst material which has been obtained by impregnation of an inorganic support with the heteropolyacid, it is believed that formation of a bond between the catalyst and the support is promoted, which can assist in controlling the leaching of catalyst into the reaction mixture. However, as a result of such interaction and bond formation, the catalyst species may be altered to some extent by such calcination, so that the value of such a post impregnation calcination tends to vary depending upon the support employed. For some supports, including alumina in particular, it is advantageous to calcine at a temperature of at least 300°C and usually not higher than about 600°C. In a number of instances, a particularly suitable temperature for post-impregnation calcination of for example alumina is at least about 400°C and especially from about 450 to about 550°C. Other supports for which post impregnation calcination is an appropriate activity include magnesium silicate and zirconium phosphate. However, when magnesium oxide or a related oxide such as calcium or zinc is employed as support, it may be preferable not to calcine the support after it has been impregnated by the heteropolyacid catalyst.

The solvent employed in the reaction mixture according to the present invention must not comprise a carboxyl group. Carboxyl-containing compounds, such as carboxylic acids, anhydrides and esters, are capable of forming peracids under the conditions employed for the reaction. Peracids are aggressive oxidants and therefore tend, particularly in the case of aldehydes, to oxidise the carbonyl compounds further than is desired. The solvent is preferably miscible with water and, although water immiscible solvents may be employed, it is believed that the use of a phase transfer catalyst, which would be advantageous to achieve an efficient process, would tend to result in the leaching of the catalyst off the support, which would reduce the desirability of the process.

In most embodiments of the present invention, the solvent employed is resistant to oxidation, by which is meant that under the conditions employed, the solvent is either not oxidised at all, or is oxidised at such a slow rate that substantially no oxidation of the solvent occurs during the reaction time employed. It will be recognised, however, that it can be desirable to employ a solvent that is less resistant to oxidation if the use of such a solvent is necessary to achieve a particular effect, for example to solubilise a particular reagent. In such cases, it is preferable that the solvent has a relatively low rate of oxidation compared to the substrate. Solvents used in the present invention are often selected from low molecular weight alcohols such as methanol, ethanol, propan-1-ol, propan-2-ol and tertiary butanol, and nitriles such as acetonitrile, of which tertiary butanol and acetonitrile are preferred.

In certain embodiments of the present invention where the substrate alcohol is liquid at the reaction temperature, the alcohol can serve as its own solvent, thus avoiding the need for the use of an additional component and reducing the process costs.

The substrate alcohols that can be oxidised by the process according to the present invention comprise a very wide group of chemicals. The group includes primary and secondary, linear, branched and cyclic aliphatic and aromatic alcohols and polyols. It will be recognised that in such a wide group, certain members of the group will be rather more readily oxidisable than others, in accordance with well established chemical principles. For example, it is well known that primary aliphatic alcohols such as octan-1-ol are rather more resistant to oxidation than secondary alcohols such as octan-2-ol, or aromatic alcohols such as benzyl alcohol, and so either more forcing conditions can be necessary, or lower yields can be expected. To some extent, the

problems of low yields can be mitigated if unreacted starting material is recovered and recycled.

Examples of aliphatic alcohols that can be oxidised by the process according to the present invention include, in addition to octan-1-ol and octan-
5 2-ol, cyclohexanol and menthol. An example of an aromatic alcohol that can be oxidised is benzyl alcohol. The aromatic group can optionally be substituted by one or more substituents, including halogens such as fluoro, chloro and bromo groups, amino groups, hydroxy groups and alkyloxy groups such as methoxy and ethoxy groups. Examples of substituted aromatic
10 alcohols that can be oxidised by the process according to the present invention include 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol and 4-fluorobenzyl alcohol.

A group of alcohols which are particularly suited to oxidation by the process according to the present invention are those which contain an
15 additional oxidation-sensitive grouping, such as a carbon-carbon double bond. Oxidation of such compounds is often difficult because the oxidant can readily attack the other functional group as well as the alcohol group. Examples of such compounds include 2-cyclohexen-1-ol and geraniol. The hydroxyl group in such compounds can readily and selectively be oxidised to carbonyl
20 compounds by the process according to the present invention.

The process according to the present invention is usually carried out at elevated temperature, typically from 50°C up to the reflux temperature of the reaction medium, and particularly from about 60 to about 85°C. Particularly
25 for substrates which boil under standard atmospheric pressure at lower temperatures than the desired reaction temperature, the reaction may be conducted at an elevated pressure selected so as to permit the desired temperature to be attained, but of course the higher boiling substrates may likewise be reacted at elevated pressure if desired.

Hydrogen peroxide can be introduced into the reaction mixture in
30 stoichiometric, sub-stoichiometric or greater than stoichiometric amounts, based on the mole ratio of hydrogen peroxide to oxidisable alcohol. It may be preferable to employ a sub-stoichiometric amount of hydrogen peroxide when the substrate is particularly sensitive to further oxidation. In most embodiments, however, it is preferred to employ at least a stoichiometric
35 amount of hydrogen peroxide, and often an excess of hydrogen peroxide, such as up to 5 moles of hydrogen peroxide per mole of oxidisable alcohol, i.e. a five times excess, and preferably from about 1.5 to about 3 moles of

hydrogen peroxide per mole of oxidisable alcohol, i.e. about a 1.5 to about a 3 times excess.

The hydrogen peroxide is preferably introduced into the reaction mixture in the form of a concentrated aqueous solution, and frequently of 5 from about 30 to 70% w/w hydrogen peroxide. Preferably, the hydrogen peroxide is introduced into the reaction mixture which contains both the substrate and catalyst system, and particularly preferably it is introduced gradually, for example over a period of from 15 minutes to 4 hours, such as in small increments or in a continuous feed.

10 The ratio of supported catalyst to substrate can be selected over a wide range of weight ratios, often in the range of from 1 : 1 to 1 : 50 and in a number of instances from 1 : 5 to 1 : 25. The ratio chosen often takes into account the loading of catalyst on the support and the activity of the substrate, as well as the other reaction conditions selected.

15 The volume of reaction medium employed is often selected in the range of from 1 to 15 volumes of solvent per volume of substrate and in many instances within the range of from 2 to 8 volumes of solvent per volume of substrate.

The overall reaction period, including the period of introduction of the 20 second reagent which is normally hydrogen peroxide, often comprises from about 2 to about 12 hours, and in many instances is from about 3 to about 8 hours. However, longer reaction periods of for example 12 to 30 hours can be employed, if desired by the user, though particularly for oxidation-resistant substrates.

25 When the oxidation process has been permitted to continue for the desired period, the reaction can be halted by physically separating the particulate catalyst from the reaction mixture by filtration or centrifugation and/or by cooling the mixture for example to ambient. The recovered catalyst can be re-employed in a further reaction mixture, possibly after 30 washing with solvent and/or drying and/or re-calcination, if desired.

Having described the invention in general terms, specific embodiments thereof are described in greater detail by way of example only.

35 Catalyst Preparation.

3g of the selected heteropolyacid was dissolved in 25ml of demineralised water. To this solution was added 20g of the selected support, and the mixture stirred at room temperature for 4 hours. The slurry was filtered, and

the residue dried in an oven at 60°C overnight. The dried solid was then calcined at 500°C for 4 hours in a muffle furnace. The catalysts produced had a nominal heteropolyacid loading of 10% by weight.

5 Example 1

Benzyl alcohol (8g, 74mmol), acetonitrile (40ml) and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /gamma Al_2O_3 (0.5g) were charged into a reaction vessel and heated to 80°C with stirring. Aqueous 35% w/w hydrogen peroxide (14.4g, 148mmol) was added over 45 minutes whilst maintaining stirring and the temperature was
10 maintained at 80°C. On completion of the hydrogen peroxide, the reaction was continued for a further 5 hours.

Analysis of the reaction mixture by gas chromatography showed that 43% of the benzyl alcohol had been converted, with a selectivity to benzaldehyde of
15 74%. The selectivity to benzoic acid was only 14%.

Comparison 2

The procedure of Example 1 was followed, except that no catalyst was employed.

20

Only a very low conversion of benzyl alcohol of 9% was achieved.

Comparison 3

The procedure of Example 1 was followed, except that no catalyst was
25 employed, and the oxidation was carried out in acetic acid as a solvent.

49% of benzyl alcohol was converted with a selectivity to benzaldehyde of only 9%, but a selectivity to benzoic acid of 90%.

30 Example 4

The procedure of Example 1 was followed, except that tertiary butanol (40ml) was employed as solvent.

36% of the benzyl alcohol had been converted, with a selectivity to
35 benzaldehyde of 72%.

Comparison 5

The procedure of Example 4 was followed, except that no catalyst was employed.

- 5 Only a very low conversion of benzyl alcohol of 15% was achieved.

Example 6

The procedure of Example 1 was followed, except that $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ (0.5g) was employed as catalyst.

10

25% of the benzyl alcohol had been converted, with a selectivity to benzaldehyde of 54%.

Example 7

- 15 The procedure of Example 1 was followed, except that $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{gamma Al}_2\text{O}_3$ (0.5g) was employed as catalyst.

53% of the benzyl alcohol had been converted, with a selectivity to benzaldehyde of 38%.

20

Example 8

The procedure of Example 1 was followed, except that the catalyst employed was recycled catalyst that was recovered from Example 1.

- 25 23% of the benzyl alcohol had been converted, with a selectivity to benzaldehyde of 85%.

Example 9

- The procedure of Example 1 was followed, except that octan-2-ol (8g, 62mmol) and 12g 35%w/w hydrogen peroxide were employed.

30

36% of the octan-2-ol had been converted, with a selectivity to octan-2-one of 81%.

- 35 Example 10

The procedure of Example 1 was followed, except that octan-1-ol (8g, 62mmol) and 12g 35%w/w hydrogen peroxide were employed.

12% of the octan-1-ol had been converted, with a selectivity to octaldehyde of 60%.

Example 11

- 5 The procedure of Example 1 was followed, except that menthol (8g, 52mmol) and 10.1g 35%w/w hydrogen peroxide were employed.

36% of the menthol had been converted, with a selectivity to menthone of 100%.

10

Comparison 12

The procedure of Example 11 was followed, except that the oxidation was carried out in acetic acid as a solvent.

- 15 Only 14% of menthol was converted.

Example 13

The procedure of Example 1 was followed, except that 4-chlorobenzyl alcohol (8g, 56mmol) and 10.9g 35%w/w hydrogen peroxide were employed.

20

47% of the 4-chlorobenzyl alcohol had been converted, with a selectivity to 4-chlorobenzaldehyde of 98%.

Comparison 14

- 25 The procedure of Example 13 was followed, except that no catalyst was employed, and the oxidation was carried out in acetic acid as a solvent.

59% of 4-chlorobenzyl alcohol was converted, but with a selectivity to 4-chlorobenzaldehyde of only 26%, but a selectivity to 4-chlorobenzoic acid of 74%.

30

Example 15

The procedure of Example 1 was followed, except that 3-hydroxycyclohexene (8g, 82mmol) and 15.9g 35% w/w hydrogen peroxide were employed.

35

100% of the 2-cyclohexen-1-ol had been converted, with a selectivity to 2-cyclohexen-1-one of 77%.

Comparison 16

The procedure of Example 15 was followed, except that no catalyst was employed, and the oxidation was carried out in acetic acid as a solvent.

- 5 No products were detected by gas chromatography, indicating that the substrate had been substantially destroyed by the oxidation.

The results of the Examples above show that the process according to the present invention gave controlled selective oxidation to aldehydes or ketones
10 for a number of substrates. The results of Comparisons 2 and 5 show that when no catalyst was employed, conversions of substrate were unacceptably low. The results of Comparisons 3 and 14 show that a similar oxidation system employing acetic acid as solvent in the absence of catalyst achieved good conversions of substrate, but the major product was the corresponding
15 acid, whereas the process according to the present invention gave the aldehyde as the major product. The result of Comparison 12 shows that changing the solvent system to acetic acid gave significantly poorer oxidation of menthol than the use of acetonitrile in Example 11. This is most surprising given the results of Comparisons 3 and 14, where the use of acetic acid
20 without the catalyst gave a more aggressive oxidation system. The result of Example 15 shows that selective oxidation of alcohols containing other oxidation sensitive groups is possible with the process according to the present invention, whereas the use of a similar system in Comparison 16 resulted in the decomposition of the substrate.

25

Claims

1. A process for the selective oxidation of alcohols wherein a substrate alcohol is contacted with hydrogen peroxide in a reaction medium in the presence of catalyst, characterised in that:
 - i. the reaction medium comprises a solvent that does not comprise a carboxyl group, and
 - ii. the catalyst comprises a heteropolyacid which is supported on an insoluble particulate support.
2. A process according to claim 1, characterised in that the heteropolyacid comprises tungsten.
3. A process according to claim 1 or 2, characterised in that the catalyst comprises a non-metallic heteroatom selected from Group IV or Group V of the periodic table.
4. A process according to claim 3, characterised in that the non-metallic heteroatom is selected from silicon or phosphorus.
5. A process according to any preceding claim, characterised in that the catalyst has the empirical formula:
$$Q_{3/n}PW_{12}O_{40}$$
when they are brought into contact with the support in which Q represents hydrogen or other counterion, and n is its basicity in the general formula.
6. A process according to any preceding claim, characterised in that the support is selected from aluminium, silicon, germanium, magnesium, titanium, tin, zinc or zirconium oxides.
7. A process according to claim 6, characterised in that support comprises silica or an activated alumina.
8. A process according to claim 7, characterised in that the support comprises gamma alumina.
9. A process according to any preceding claim, characterised in that the solvent comprises low molecular weight alcohols or nitriles.

10. A process according to claim 9, characterised in that the solvent comprises tertiary butanol or acetonitrile.
11. A process according to any one of claims 1 to 8, characterised in that the substrate alcohol also serves as solvent.
12. A process according to any preceding claim, characterised in that the oxidation is carried out at a temperature of from 50°C to the reflux temperature of the reaction medium.
13. A process according to any preceding claim, characterised in that the hydrogen peroxide is employed at a mole ratio to substrate alcohol of from stoichiometric to about a five times excess.
14. A process according to claim 13, characterised in that the mole ratio of hydrogen peroxide to substrate alcohol is from about a 1.5 to about a 3 times excess.
15. A process according to any preceding claim, characterised in that the weight ratio of catalyst to substrate alcohol is from about 1 : 1 to about 1 : 50.
16. A process according to claim 15, characterised in that the weight ratio of catalyst to substrate alcohol is from about 1 : 5 to about 1 : 25.
17. A process according to any preceding claim, characterised in that the hydrogen peroxide solution employed has a concentration of greater than about 30% w/w.
18. A process according to any preceding claim, characterised in that the substrate alcohol is selected from the group comprising primary and secondary, linear, branched and cyclic aliphatic and aromatic alcohols and polyols.
19. A process according to claim 18, characterised in that the substrate alcohol is selected from the group comprising octan-1-ol, octan-2-ol,

benzyl alcohol, 4-chlorobenzyl alcohol, 4-fluorobenzyl alcohol, 4-methoxybenzyl alcohol, menthol, 2-cyclohexen-1-ol and geraniol.

20. A process for the selective oxidation of alcohols with hydrogen peroxide substantially as described herein with reference to any one of the Examples.
21. A process for the selective oxidation of alcohols with hydrogen peroxide substantially as described herein with reference to any novel feature or combination of features.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 94/00441

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07C45/29 B01J27/188 B01J31/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 00338 (SOLVAY INTEROX LIMITED) 7 January 1993 see claims	1-21
Y	US,A,4 259 527 (F. MARES ET AL.) 31 March 1981 see claims	1-21
Y	EP,A,0 232 742 (ISTITUTO GUIDO DONEGANI S.P.A.) 19 August 1987	1-21

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 April 1994

Date of mailing of the international search report

- 2. 05. 94

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/GB 94/00441

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9300338	07-01-93	CA-A- 2111696	07-01-93
US-A-4259527	31-03-81	US-A- 4171313	16-10-79
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